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Article

The present state of lead (Pb) and zinc (Zn) contamination in agricultural soil as revealed by meta-analytic findings

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Abstract: Agricultural soil serves as the fundamental resource for grain production, with its quality being integral to both the national economy and the well-being of the population. As economic and societal development progresses, the levels of lead (Pb) and zinc (Zn) in farmland soil are on the rise. Currently, research into the total quantities and speciation distribution of Pb and Zn in agricultural soil, as well as their influencing factors, is fragmented, and there is a gap in comprehensive understanding regarding the transformation mechanisms and pollution status of various forms of these heavy metals. To gain a clearer picture of the heavy metal pollution in soil, as well as the distribution and transformation dynamics of different forms, this study conducts an integrated analysis of the pollution levels, speciation distribution, and influencing factors of Pb and Zn in Chinese farmland soil. Additionally, it assesses the ecological risk of heavy metals using principal component analysis and the geoaccumulation index. The findings indicate that the average concentrations of Pb and Zn are 4045 mg/kg and 10699 mg/kg, respectively. The residual form of Pb is most predominant in the Northwest, while the exchangeable form is most prevalent in the Southwest. The residual form of Zn constitutes over 50% of its presence. The analysis reveals that pH is the primary factor influencing the speciation distribution of heavy metals. The combined results of the geoaccumulation index and the potential ecological risk index (RI) suggest that Pb levels at the study site exceed those of Zn, though both are classified as posing a slight risk. A holistic analysis of soil environmental factors reveals that the speciation distribution of heavy metals reaches an equilibrium state through the interaction of multiple factors.

Keywords: farmland soil; heavy metals; pollution assessment; morphological distribution; influence factor

Soil is an important medium for human survival. Farmland soil is an important material basis for food production. Soil quality is directly related to social sustainable development. In recent years, due to the long-term application of chemical fertilizer [1] in farmland and the unreasonable discharge of industrial waste, heavy metals are deposited on the soil surface, resulting in heavy metal pollution [2], which has become a more prominent soil pollution problem [3]. The content of harmful heavy metals in the soil due to human activities exceeds the soil background value, resulting in heavy metal pollution, which not only affects the safety of drinking water and endangers human health, but also in the heavy metal polluted soil, the content of heavy metals in plants exceeds the standard, plant growth is inhibited, and the quality of agricultural products is reduced, thus posing a potential threat to food production and food safety [4]. At present, the world's average annual emissions are about 150,000 tons of Hg, about 3.4 million tons of Cu, about 5 million tons of Pb and about 1 million tons of Ni [5]. The study [6,7] found that the toxicity and bioavailability of heavy metals are related to their total amount, existing forms and environmental conditions, such as pH, total organic carbon (TOC) and cation exchange capacity (CEC). Different geochemical environments determine different forms of heavy metals [8]. Therefore, studying the existing forms, migration and transformation mechanisms of heavy metals has a far-reaching impact on predicting the toxic effects of heavy metals on the environment [9].

Research [10] shows that Tessier method is a common method for analyzing the forms of heavy metals, which can be divided into exchangeable state, carbonate bound state, iron manganese oxide bound state, organic bound state and residual state. The physical and chemical properties of soil, such as the total amount of heavy metals in soil, soil organic matter (SOM), cation exchange capacity (CEC), redox potential (EH), iron and manganese oxides, pH and carbonate, soil texture, are closely related to the distribution of heavy metals. According to the bulletin of national soil pollution investigation, Pb and Zn are the heavy metals accumulated in the soil. Many people have also done a lot of experimental analysis and Research on the forms and influencing factors of Pb and Zn, but it is difficult to reflect the unified law between the forms and influencing factors. Meta analysis is used to summarize the single research published on a subject in a more reliable way, so as to illustrate a unified law or effective result [11]. Lei [12] collected data of 249 heavy metals in farmland soil and analyzed the current situation of heavy metal pollution in farmland soil; Net et al. [13] analyzed the toxicity characteristics, morphological distribution and migration law of pollutants (phthalates) in the environment with mate. Therefore, this paper takes Pb and Zn as the research objects to collect and sort out the literature data, analyze the mechanism of heavy metal speciation transformation in soil, and understand the decisive factors of heavy metal ecotoxicity, in order to provide a useful supplement and improvement to the theory of heavy metal migration and transformation.

1. Data sources and research methods

1.1. Data sources

The data came from CNKI, wanfang and VIP, etc. To collect the spatial and temporal distribution information of Pb and Zn in the soil of natural farmland, mining areas and sewage irrigation areas in nearly 30 provincial administrative regions of the country (except Tibet Autonomous Region, Xinjiang Uygur Autonomous Region, Hong Kong Special Administrative Region, Macao Special administrative region and Taiwan region), including soil properties, total amount of Pb and Zn, and the absolute and relative contents of various heavy metal forms. Based on the keywords of farmland soil, Pb, Zn, morphological distribution and total amount, 159 literatures and 381 sampling points were retrieved. According to the geological landform, soil type, land use mode, natural resource status and climate, the soil was divided into four regional groups, namely North China Northeast Group, northwest group, south China East China group and southwest group.

According to the different research methods of heavy metal forms in the literature, the forms of heavy metals are divided into five categories, that is, the water-soluble and exchangeable states are classified as exchangeable states; carbonate bound state is carbonate bound state; iron manganese oxide bound state, amorphous iron oxide bound state, crystalline iron oxide bound state, hydroxide precipitation absorption state or adsorption state and iron manganese bound state are classified as iron manganese oxide bound state; organic bound state, organic state, loosely bound organic state, tightly bound organic state, macromolecular humus bound state, sulfide precipitated state, etc. Are classified as organic bound state; other remaining forms are uniformly classified as residual state [14–16]. The data shall be standardized according to the data processing method of Zhengzhou [17].

1.2. Research methods

The geological accumulation index method is used to evaluate the accumulation of heavy metals, taking into account the impact of human pollution factors, geochemical background values and natural diagenesis on the background values, which can directly reflect the level of heavy metal pollution [18]. The calculation expression is:

$$I_{\text{geo}} = \log_2\left[C_n / \left(K \cdot B_n\right)\right] \quad (1)$$

where: C_n refers n to the content of elements B_n in n sediments; is the geochemical background k value of elements; it is the variation coefficient of background value that may be caused by rock difference (generally 1.5). Generally, the I_{geo} pollution level is divided into the $I_{\text{geo}} < 0$ following levels: level 0, $I_{\text{geo}} < 1$ no pollution; class 1, between no pollution and moderate $I_{\text{geo}} < 2$ pollution; level 2, medium pollution; $I_{\text{geo}} < 3$, Grade 3, between medium pollution and heavy pollution; $I_{\text{geo}} < 4$, Level 4, heavy pollution; $I_{\text{geo}} < 5$, grade 5, between heavy pollution and extremely heavy pollution; $I_{\text{geo}} < 6$, grade 6, extremely heavy pollution [12].

The potential ecological risk index (RI) method was proposed by Hakanson, a Swedish geochemist, from the perspective of sedimentology. It is one of the most commonly used methods to evaluate the degree of heavy metal pollution [19]. The potential ecological risk index is calculated by determining the toxicity coefficient. See Equation (2) and Equation (3) for calculation of potential ecological hazard coefficient of single heavy metal and comprehensive potential ecological hazard index of multiple heavy metals.

$$E_r^i = T_r^i \cdot \left(C_{measure}^i / C_n^i\right) \quad (2)$$

$$\text{RI} = \sum E_r^i \quad (3)$$

Where: E_i^rIs the potential ecological hazard coefficient of heavy metal I; T_i^rIs the Toxicity Coefficient of heavy metal I; $C_{measure}^i$Is the measured value of heavy C_n^imetal I; is the evaluation standard mass concentration of heavy metal I. According to GB 15618-2018 soil environmental quality screening standard for soil pollution risk of agricultural land [20]; r i is the comprehensive potential ecological hazard index of various heavy metals, and the corresponding classification is shown in Table 1. Excel 2010, spss 230, origin 2017 and ArcGIS 102 were used to analyze and map the data.

Table 1. Classification of potential ecological risk index of heavy metals.

Grade	E_i^r	RI	Hazard degree
I	≤ 40	≤ 90	Minor hazard
П	> 40~80	> 90~180	Moderate hazard
Ш	> 80~160	> 180~360	Strong hazard
IV	> 160~320	> 360~720	Strong hazard
V	> 320	> 720	Extreme hazard

2. Results and analysis

2.1. Soil pb and Zn concentration level

Figure 1 shows the statistical chart of Pb and Zn contents in the soil of the study area. According to GB 15618-2018 soil environmental quality agricultural land soil pollution risk control standard and the distribution characteristics of acidified pH of Chinese farmland soil [21], pH = 6.5 is used as the screening and control standard for soil pollution risk of agricultural land in the north and south. In **Figure 1**, there are 379 points of Pb in a, with an average content of 40.45 mg·kg^{-1}. The northern points are all less than the screening value, which is a safe and pollution-free risk level; in the southern sites, the proportion of exceeding the screening value in the South China East China group and the southwest group is similar, which are 9.30% and 10.42% respectively, but both are less than the control value. In **Figure 1**, there are 276 points of Zn in B, with an average content of 106.99 mg·kg^{-1}. Its distribution characteristics in the north are similar to that of Pb, and the contents are all less than the screening value; some points in the South exceeded the screening value. The over standard rates of South China East China group and southwest group were 16.22% and 6.45% respectively. The content in South China East China was significantly higher than that in other regions but lower than the control value. It indicates that the contents of Pb and Zn are generally safe at the research sites, and only a few sites have certain health risks.

2.2. Geological accumulation index evaluation

The relationship between geological accumulation index and pollution level is shown in **Table 2** through the calculation of Pb and Zn geological accumulation index at the research point. It can be seen that the Pb geological accumulation index ranges from −4.42 to 4.24, the average pollution index is −0. 18, and 57. 8% of the research sites are grade 0, which is no pollution; 21.5% of the research sites are of grade 1, ranging from no pollution to medium pollution; grade 2, 3, 4 and 5 account for 11.8%, 7.5%, 3.9% and 0.8% respectively, belonging to the pollution level. Among them, Guangxi, Yunnan, Fujian, Guizhou, Jiangxi and Hunan have high Pb accumulation index and serious soil accumulation. The geological accumulation index of Zn ranges from -0.43 to 2.55, and the study site with an average pollution index of 018578% is grade 0, which is pollution-free; 295% of the research sites are level 1, ranging from no pollution to medium pollution; grade 2 and 3 account for 8.2% and 4.5% respectively, belonging to the pollution level. Among them, the geological accumulation index of Zn in Guangxi, Fujian and Liaoning is higher. In general, the geological accumulation index of Zn is lower than that of Pb, which indicates that the ecological risk of Pb is high.

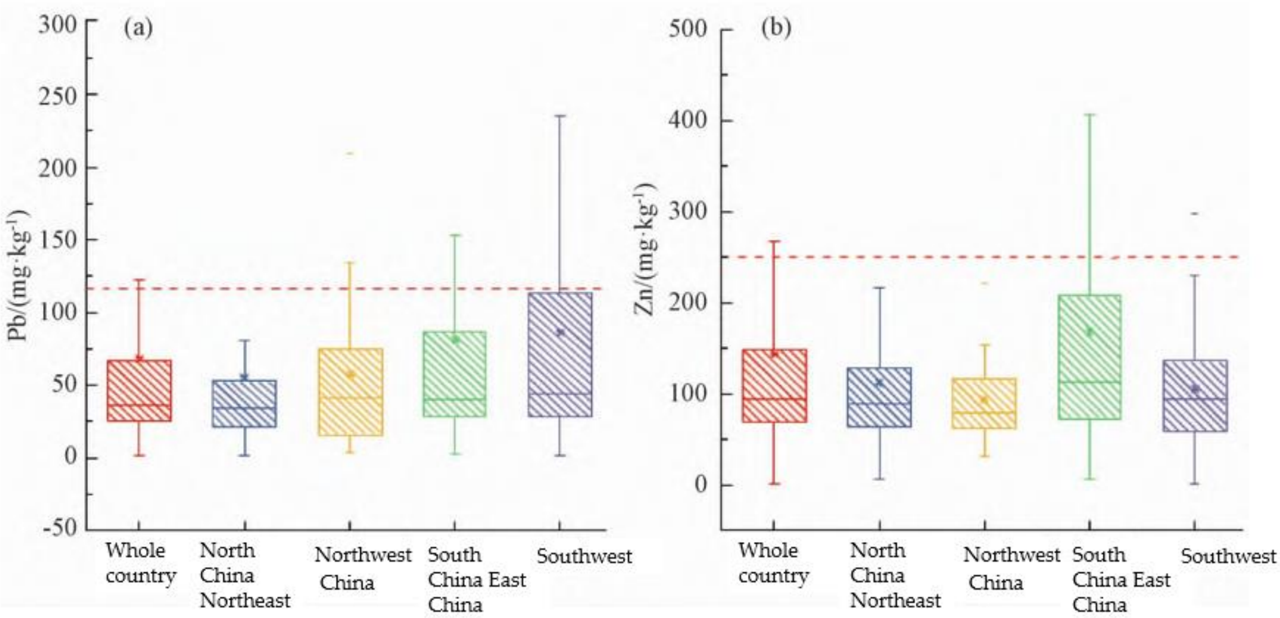

Figure 1. Distribution of Pb and Zn contents in soil.

Table 2. Geological accumulation index of heavy metals in soil.

Heavy metal	Minimum value	Maximum	Mean value	Variance	Proportion of each pollution level/%					
					0	1	2	3	4	5
Pb	−4.42	424	0.28	145	43.6	215	118	75	39	08
Zn	−0.43	2.55	−0.18	114	57.8	29.5	82	4.5	—	—

Table 3. Evaluation results of potential ecological risk index.

Index	Minimum value	Maximum	Mean value	Variance	Hazard level				
					Slight	Secondary	Strong	Strong	Extremely strong
E_i^r of Pb	069	25.82	409	555	100	0	0	0	0
E_i^r of Zn	003	297	060	046	100	0	0	0	0

2.3. Potential risk assessment

See **Table 3** for potential ecological risk indexes EI and RI of Pb and Zn at the research site. It can be seen that the EI of Pb is 069~2582, and the average index is 409, both of which are slight hazards. The EI of Zn is 003~297, and the average index is 06, all of which are slight hazards. Through the comprehensive evaluation of RI results, it is found that the comprehensive potential ecological risk index ranges from 072 to 2879, with an average of 452, indicating that the risk degree of heavy metals at the research site is a slight hazard.

RI	072	2879	452	560	100	0	0	0	0

3. pb and Zn speciation distribution

3.1. Speciation characteristics of pb and Zn in soil

Figure 2a shows the distribution of Pb occurrence forms. Nationwide, the highest proportion of residual state in all research sites is 4059%. Among the effective States, the bound state of iron manganese oxide is 2652%, which is much higher than the other three forms, while the exchangeable state and carbonate bound state with strong activity are 965% and 854% respectively. In general, most of Pb exists in the effective state. In terms of regional distribution, the highest proportion of residual state in Northwest China is 4502%, indicating that heavy metals in this region mainly come from natural geological weathering, with relatively weak mobility and biological toxicity. The distribution of iron manganese oxide bound state and organic bound state in the four regions is similar. The carbonate bound state in North China Northeast China is 1176%, much higher than that in South China, while the exchangeable state in Southwest China is 1485%, the highest in China, this may be related to the background value of high pH soil in the north than in the South [21].

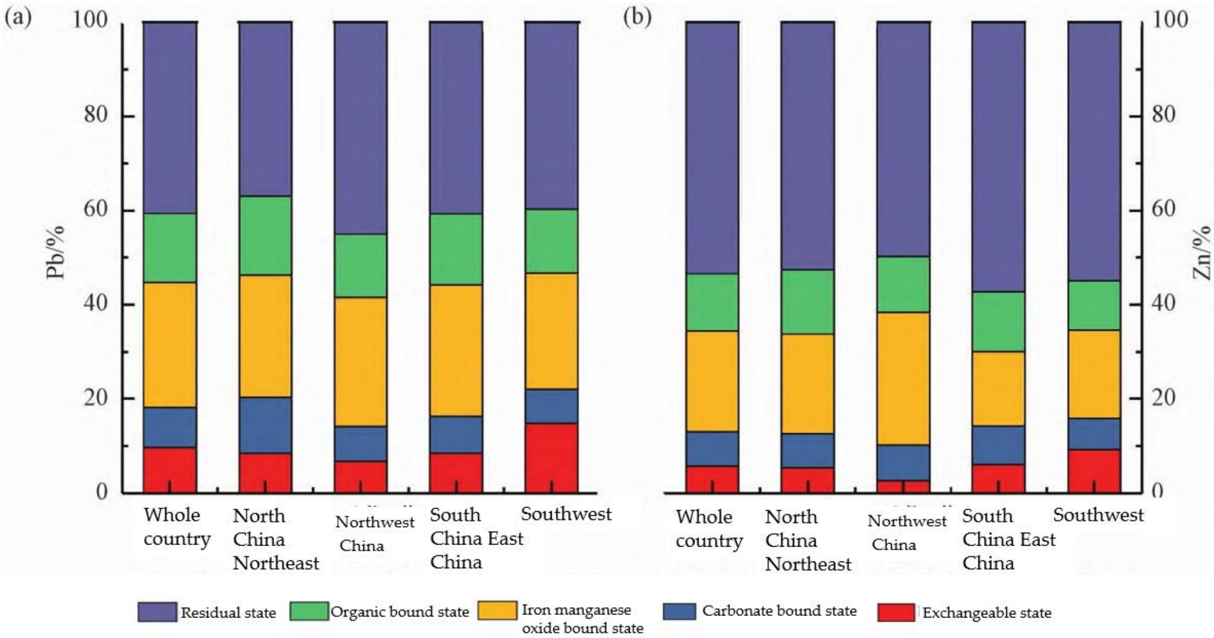

Figure 2. Speciation distribution of Pb and Zn in soils of China.

In **Figure 2b** shows the distribution of Zn occurrence form. The distribution of Zn is similar to that of Pb, and the residual state is the highest among the five forms, accounting for 5343%. The proportion of exchangeable state and carbonate bound state with strong activity in the available state is much lower than that of iron manganese oxide bound state and organic bound state, which are 575% and 734% respectively, of which the iron manganese oxide bound state is 2134%, which may be related to the parent material of soil formation. From the perspective of zoning, the proportion of residual state in the four regions reached or exceeded 50%, and the exchange state in the northwest region was only 262%, which was far lower than that in the other three regions, while the organic bound state reached 2834%. The exchangeable state accounts for 927% in the southwest, which is much higher than that in the north, which may be related to the low pH in the south.

3.2. Influencing factors of pb and Zn speciation distribution in soil

The adsorption characteristics and morphological characteristics of heavy metals on the surface of soil minerals are closely related to soil physical and chemical properties, such as pH, cation exchange capacity (CEC) and soil organic matter (SOM). Different physical and chemical properties can promote the mutual transformation of heavy metals among various forms, thus indirectly affecting the bioavailability of heavy metals [22]. Pearson correlation analysis was used to statistically analyze the relationship between soil physical and chemical properties (pH, cec, som) and Pb, Zn, and to evaluate the impact of soil properties on the distribution of heavy metal forms. The results are shown in **Table 4**.

Table 4. Correlation Analysis between heavy metal forms and soil properties.

Soil Nature	Heavy metal	Form			
		Commutative state	Carbonate bound state	Iron manganese oxide bound state	Organic bound state
Ph	Pb	−0.143	0.188**	0.002	0.162*
	Zn	−0.210*	0.100*	0.320**	0.160*
CEC	Pb	−0.310*	−0.160	0.320**	0.180
	Zn	−0.177	0.045	0.511**	0.064
SOM	Pb	−0.124	−0.101	−0.134*	0.161*
	Zn	0.059	0.082	0.101	0.065*

Note: *- significant correlation at 0.05 Level; ***- Significant correlation at 0.01 Level.

It can be seen from **Table 4** that the soil pH at the research site is negatively correlated with the exchangeable state of Pb and Zn, of which the correlation with Zn is significant, while the correlation with carbonate bound state is extremely significant and positively correlated with Pb and Zn respectively. It indicates that the soil pH decreases and the content of active Pb and Zn increases [23]. It may be that the decrease of soil pH increases soil h+, which forms a competitive adsorption with the metal cations adsorbed on the surface of soil colloid, so that the heavy metals are desorbed. As the soil pH increases, the positive charge on the surface of the soil colloid decreases and the adsorption capacity for Zn increases [24], so the content of Zn increases. Other studies suggest that the decrease of pH increases h+, h+ replaces soluble metal cations, combines with Oh, co2, s2 and phosphate, and the potentially available carbonate bound state will be activated and transformed into exchangeable state [25]. When the pH value of the system is high, carbonate can directly combine with heavy metals to form precipitation [26]. PH is positively correlated with the binding state of Pb and Zn iron and manganese oxides, and it is highly significantly positively correlated with Zn, indicating that the high energy of pH rise greatly increases the existence of the binding state of iron and manganese oxides. The study found that pH has an important impact on the binding state of iron and manganese oxides. The increase of pH is conducive to the formation of iron and manganese oxides [21]. The negative charge content on the surface of oxidized substances in soil increases with the increase of pH [27]. The adsorption of heavy metals changes from ordinary adsorption to specific adsorption, enhanced the stability of iron manganese oxide bound heavy metals [28]. The organic bound state of Pb and Zn is significantly positively correlated with pH, indicating that the increase of pH is conducive to the existence of organic bound state. The study found that the increase of pH promotes the decomposition of organic matter [29], increases the soluble organic matter (DOM), and enhances the stability of the complex formed with heavy metals.

Cation exchange capacity (CEC) refers to the capacity of cations adsorbed and exchanged by soil. In the study site, cec has a significant negative correlation with Pb, and a negative correlation with Zn, but not significant. However, it has a very significant positive correlation with the bound state of Pb and Zn Fe Mn oxides. The study found that the higher the CEC, the more pb2+ adsorbed by the soil, and the CEC has a significant negative correlation with the equilibrium concentration of heavy metal ions [30,31]. Bolan et al. [32] applied sludge to increase soil CEC, which is conducive to the stability of heavy metals.

Soil organic matter is a carbon containing substance in soil. Humus in soil can combine heavy metals through adsorption, complexation and chelation. It can be seen from **Table 4** that Pb exchange state and iron manganese oxide bound state have a negative correlation with organic matter (SOM) and a positive correlation with carbonate bound state and organic bound state, in which the positive correlation with organic bound state is significant, indicating that the greater the content of organic matter, the lower the content of heavy metals in exchange state and iron manganese oxide bound state [33,34], and the higher the content of organic bound heavy metals, it may be that organic matter can complex heavy metal ions and attach to the surface of soil particles, which can enhance the adsorption capacity of heavy metals [35]. The contents of carbonate bound and residual heavy metals did not change significantly. However, the correlation of various forms of Zn is not significant, indicating that soil organic matter is a complex system. Ma et al. [36] found that acid soil contains high content of organic matter, accompanied by high migration performance of heavy metals. Therefore, the content of organic matter can not fully reflect the influence of organic matter on the speciation of heavy metals. The components of soil organic matter are also closely related to the forms of heavy metals in soil. Soluble organic matter such as humus can combine with heavy metals to form soluble metal complexes. Organic matter can promote and inhibit the migration of heavy metals. For example, Jing et al. [37] focused on the distribution of dissolved organic matter (DOM) and particulate organic matter (POM) in soil. Tipping et al. [38] and Bada et al. [39] found that soluble organic matter can significantly enhance the mobility of Ni, pb, cu and Zn. Gambrell et al. [15] found that macromolecular insoluble organic matter can reduce the bioavailability of heavy metals.

3.3. Comprehensive analysis of soil properties

A large number of literature studies also show that the form distribution of heavy metals is not only affected by a single factor, but also may be affected by many factors, including the accumulation of heavy metals in soil, ph, som and CEC. In **Figure 3**, principal component analysis (PCA) is used to comprehensively analyze the internal relationship between various factors. The variance contribution rate of the first principal component factor (PC1) is 3873%, and the characteristic factors Pb and Zn have high positive load on the first principal component, which are 0870 and 0904 respectively, while pH has high load on the first principal component, which is -0517. Other literatures reported that long-term application of chemical fertilizer, organic fertilizer, phosphate fertilizer, etc. [40–45] in most parts of China not only caused significant accumulation of heavy metals in soil, but also led to the decline of soil pH [46–48]. Therefore, the first principal component represents the impact of human factors such as fertilization on soil pH and total heavy metals. The variance contribution rate of the second principal component factor (PC2) is 2876%, and the characteristic factors CEC and SOM have high positive loads on the second principal component, which are 0.874 and 0858 respectively, mainly reflecting the impact of temperature and humidity on soil organic matter and soil texture. The study [49] found that when the humidity is 60%~65% and the temperature is 45 ℃~50 ℃, the decomposition of organic matter is the most sufficient, which can reach 90% of the total amount. If these ranges are exceeded, the mineralization of organic matter is blocked, which can promote the formation of humus. According to the comprehensive analysis, the two principal components reflect the overall reliability of 6749%, which indicates that human factors and climate factors are the two key factors affecting the distribution of heavy metal forms, and indirectly affect the soil environmental factors, which reach a dynamic balance with the soil chemical reaction [50], and the forms can be transformed into each other.

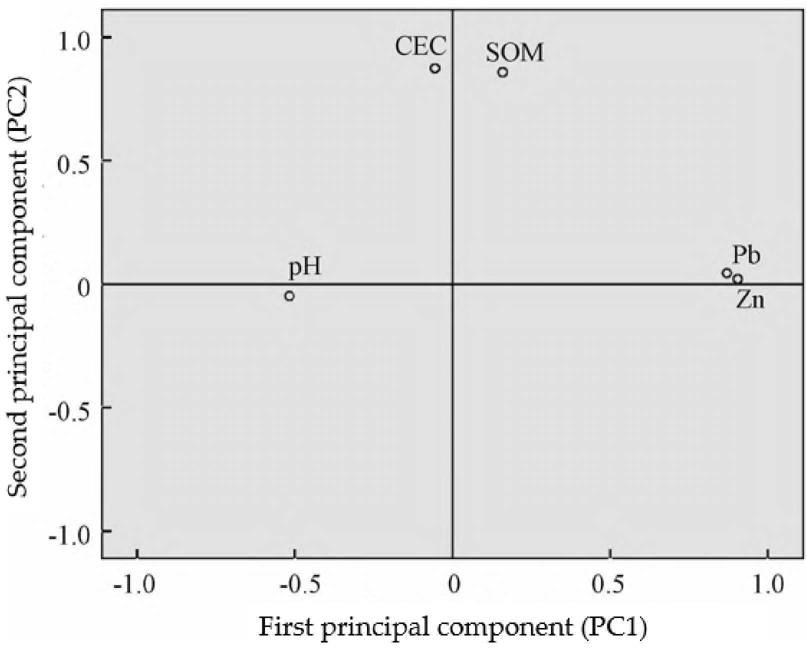

Figure 3. Principal component analysis—factor load.

4. Summary

According to the statistical analysis of the data of research sites nationwide, the total average value of Pb content in soil is 4.045 mg·kg^{-1}. The content in North China northeast and Northwest China is lower than that in the south, and is within the screening value of agricultural land soil pollution risk; the total average content of Zn in soil is 106.99 mg·kg^{-1}, and the regional distribution is highly similar to that of Pb.

Pb at the research site mainly exists in the effective state (exchangeable state, carbonate bound state, iron manganese oxide bound state, organic bound state), accounting for 5941%; the residual state of Zn accounts for 53.43% of the five forms. In terms of regional distribution, the highest proportion of residual state in Northwest China is 45.02%, and that of carbonate bound state in North China Northeast China is 11.76%, which is much higher than that in South China, while that of exchangeable state in Southwest China is 14.85%, which is the highest in China; the residual state of Zn accounts for 50% or more in the four regions, and the exchange state in the northwest region is only 2.62%, which is far lower than that in the other three regions, while the reducible state reaches 28.34%. The proportion of exchangeable states in Southwest China is 9.27%, much higher than that in North China. Overall, the ecological risk of heavy metals in the south is higher than that in the north.

Among the effects of pH, CEC and SOM on the distribution of available states of heavy metals, the correlation between pH and Pb, Zn forms is stronger than that of CEC and SOM, and is negatively correlated with the exchange states of heavy metals and positively correlated with other available states. CEC has a very significant positive correlation with the iron manganese oxide bound state, but not with the carbonate bound state. There is a significant correlation between SOM and the speciation of heavy metals, indicating that pH is the main factor affecting the speciation distribution of heavy metals. However, the morphological distribution may not be the result of a single factor, but may be the result of a variety of factors.

The geological accumulation index shows that the average geological accumulation index of Pb is higher than that of Zn, and the pollution-free ratio is 4.36% and 5.78% respectively, indicating that the soil accumulation of Pb in the study site is stronger than that of Zn, while the potential ecological risk index EI and RI show that the hazard level of heavy metals in the study site is slight. From the perspective of principal component analysis, human factors and climate factors are the two key factors that affect the distribution of heavy metal forms, and then indirectly affect soil environmental factors. According to the dynamic balance mechanism of soil chemical reaction, the forms can be transformed into each other. Measures should be taken to guide heavy metals from active state to potential active state.

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